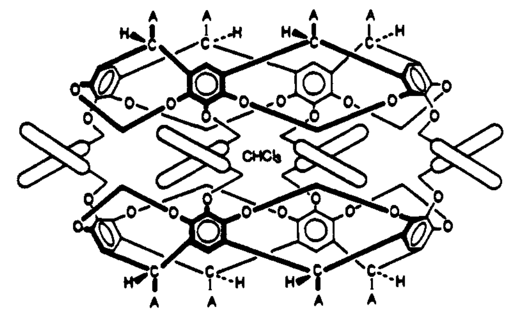
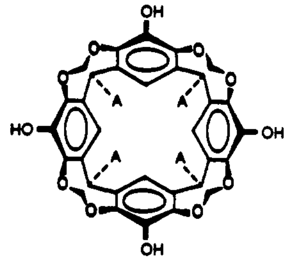
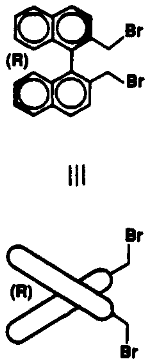


$(R)_4$-**1**·$CHCl_3$, A = $CH_2CH_2C_6H_5$



2, A = $CH_2CH_2C_6H_5$



(R)-**3**

$(CH_3)_2C_6H_4$, 3 h; $CH_3CHICH_2CH_3$, ≈50 000 h; $CH_3CHOHCH_2CH_3$, 2 h; $BrCH_2CH(CH_3)_2$, 0.33 h. The CH_3 protons in the ^{1}H NMR spectrum of **1**·1,4-$(CH_3)_2C_6H_4$ are moved by incarceration upfield by 4 ppm and the ArH protons by 2 ppm. A CPK molecular model of **1**·1,4-$(CH_3)_2C_6H_4$ can be constructed only with the long axes of each component coincident. Molecular model examination suggests that guest replacement occurs via four chiral equatorial portals generated by increasing the dihedral angles of the four binaphthyls.

For chiral selectivity studies during guest release, 1:1 hemicarceplexes were prepared.[8] From enantiomerically pure (S)-$BrCH_2CH(CH_3)CH_2CH_3$[9] were obtained $(R)_4$-**1**·(S)-$BrCH_2CH(CH_3)CH_2CH_3$[2] and $(S)_4$-**1**·(R)-$BrCH_2CH(CH_3)CH_2CH_3$.[2] The first-order rate constant for guest release[10] for the $(R)_4$-(S) isomer was (4.4 ± 0.3) × 10^{-2} h^{-1}, and for the $(S)_4$-(S) isomer it was (6.2 ± 0.3) × 10^{-3} h^{-1}, to provide $k_{R_4S}/k_{S_4S} = 7$.

From $(S)_4$-**1**·$CHCl_3$ and racemic $BrCH_2CH_2CHBrCH_3$ was prepared[8] a mixture of diastereomeric complexes (99% yield) in which one diastereomer dominated by a factor that varied in three identical runs from 1.5:1 to 2:1, reflecting a difference in free energies of association for the diastereomeric complexes of ~300 cal mol^{-1} at 100 °C.[11] The dissociation rate constants[10] were k_{fast} = (3.0 ± 0.7) × 10^{-1} h^{-1} and k_{slow} = (5.8 ± 0.5) × 10^{-2} h^{-1} to give $k_{fast}/k_{slow} = 5$. The *less* thermodynamically stable isomer provided the *faster* rate. Similarly, from $(S)_4$-**1**·$CHCl_3$ and racemic $BrCH_2CHBrCH_2CH_3$ was prepared[8] an equilibrated diastereomeric mixture in a ratio of 2:1. The dissociation rate constants[10] were k_{fast} = (1.21 ± 0.06) × 10^{-2} h^{-1} and k_{slow} = (1.3 ± 0.4) × 10^{-3} h^{-1} to give $k_{fast}/k_{slow} = 9$. The *more* stable diastereomer provided the faster rate.

The $\Delta\Delta G^{*}$ values at 23 °C for the diastereomeric complexes dissociating were as follows: for $BrCH_2CH(CH_3)CH_2CH_3$, 1.1 kcal mol^{-1}; for $BrCH_2CH_2CHBrCH_3$, 1.0 kcal mol^{-1}; for $BrCH_2CHBrCH_2CH_3$, 1.3 kcal mol^{-1}. The $\Delta\Delta G^{\circ}$ values at 100 °C for the latter diastereomers are ~300 cal mol^{-1}. Usually, $\Delta\Delta G^{\circ}$ values for diastereomeric complexes decrease with increasing temperature.[12] If in the present study $\Delta\Delta G^{\circ}$ remained at ~300 cal mol^{-1} at 23 °C, the $\Delta\Delta G^{*}$ value for the *complexation diastereomeric transition state* would be 1.6 kcal mol^{-1} for $BrCH_2CHBrCH_2CH_3$ ($k_{fast}/k_{slow} \sim 15$) and 0.7 kcal mol^{-1} for $BrCH_2CH_2CHBrCH_3$ ($k_{fast}/k_{slow} \sim 3$).

Differences in steric repulsions in the diastereomeric transition states are probably responsible for the chiral selectivity in decomplexation. With each of the three chiral guests examined, the host discriminates between the steric requirements for CH_3 vs Br, or CH_3CH_2 vs $BrCH_2$. The relative sizes of covalently bound CH_3 and Br calculated from their volumes[13a] and surface areas[13b] differ by only 5–10%. The thermodynamic stereoselectivity of $\Delta\Delta G^{\circ} \sim 300$ at 100 °C observed for the enantiomeric dibromides approximates that shown by Collet's chiral cyclotriveratrylene-based cryptophanes binding CHFClBr ($\Delta\Delta G^{\circ}$ = 260 cal mol^{-1} at 56 °C).[14]

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(8) Enantiomers of **1**·$CHCl_3$ (8–15 mg) dissolved in 2.5–15 g of guest were heated to 100 °C for 18 h in the dark. The solutions were cooled and filtered into 30–50 mL of pentane. The precipitate was collected, washed, and dried (25 °C, 10^{-2} Torr, 2 h).

(9) Aldrich Chemical Co., Milwaukee, WI, 1989–1990 catalog, p 555.

(10) The disappearance of hemicarceplex ^{1}H NMR (500 MHz, $CDCl_3$, 23 °C) spectral signals was followed. The signal integral for each point was compared with that of the 7,7′-binaphthyl protons at δ 7.6, whose clear multiplet was essentially guest independent. For the isomers of **1**·$BrCH_2CH(CH_3)CH_2CH_3$, the complexed host signal disappearance for the inward-turned OCH_2O proton at δ 4.31 (doublet) was employed (six or seven points, R^2 = 0.998, both isomers). In the thermodynamic determinations and kinetic resolution of the isomers of **1**·$BrCH_2CH_2CHBrCH_3$, the bound guest doublet signals at δ −2.07 and −1.70 (CH_3) were employed (five points, R^2 = 0.999 for the rapidly and 0.997 for the slowly dissociating isomer). Similarly, for the isomers of **1**·$BrCH_2CHBrCH_2CH_3$, the bound guest triplets of CH_3 at δ −3.01 and −2.86 were employed (eight points, R^2 = 0.999 for the rapidly and 0.947 for the slowly dissociating isomer).

(11) Times that varied from 0.75, 1, 24, and 336 h gave ratios between the above limits, showing that equilibrium was established.

(12) For example, see: Kyba, E. P.; et al. *J. Am. Chem. Soc.* **1978**, *100*, 4555–4568.

(13) (a) Gavezzotti, A. *J. Am. Chem. Soc.* **1964**, *68*, 441–451. (b) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441–451.

(14) Canceill, J.; Lacombe, L.; Collet, A. *J. Am. Chem. Soc.* **1985**, *107*, 6993–6996.

Stable η^4-Silatrimethylenemethane Transition-Metal Complexes by the Reaction of Alkylidenesilirane with Metal Carbonyl

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The coordination of transition metals has been well-known to stabilize many reactive species, e.g., carbenes, carbynes, cyclobutadiene, and trimethylenemethane. By analogy along this line, remarkable progress has been made in the synthesis of stable transition-metal complexes of unsaturated silicon species, e.g., silylene ($L_nM{=}SiR_2$),[1a–h] silene ($L_nM[\eta^2\text{-}R_2C{=}SiR_2]$),[1i–k] and disilene ($L_nM[\eta^2\text{-}R_2Si{=}SiR_2]$)[1l–n] complexes, respectively. Recently we have found the reaction of allene episulfide (II, X =

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(1) For silylene complexes: (a) Straus, D. A.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 5872. (b) Zybill, C.; Muller, G. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 669. (c) Zybill, C.; Wilkinson, D. L.; Muller, G. *Ibid.* **1988**, *27*, 583. (d) Zybill, C.; Muller, G. *Organometallics* **1988**, *7*, 1368. (e) Ueno, K.; Tobita, H.; Shimoi, M.; Ogino, H. *J. Am. Chem. Soc.* **1988**, *110*, 4092. (f) Zybill, C.; Wilkinson, D. L.; Leis, C.; Muller, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 203. (g) Tobita, H.; Ueno, K.; Shimoi, M.; Ogino, H. *J. Am. Chem. Soc.* **1990**, *112*, 3415. (h) Straus, D. A.; Grumbine, S. D.; Tilley, T. D. *Ibid.* **1990**, *112*, 7801. For silene complexes: (i) Campion, B. K.; Heyn, R. H.; Tilley, T. D. *J. Am. Chem. Soc.* **1988**, *110*, 7558. (j) Campion, B. K.; Heyn, R. H.; Tilly, T. D. *Ibid.* **1990**, *112*, 4079. (k) Koloski, T. S.; Carroll, P. J.; Berry, D. H. *Ibid.* **1990**, *112*, 6405. For a disilene complex: (l) Pham, E. K.; West, R. *J. Am. Chem. Soc.* **1989**, *111*, 7667. (m) Pham, E. K.; West, R. *Organometallics* **1990**, *9*, 1517. (n) Berry, D. H.; Chey, J. H.; Zipin, H. S.; Carroll, P. J. *J. Am. Chem. Soc.* **1990**, *112*, 452.

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S) with metal carbonyls (ML_n=$Fe_2(CO)_9$) to provide in a unique manner the first η^4-thiatrimethylenemethane complexes (I, X = S)[2a] (Scheme I). The discovery of this synthetic pathway prompted us to extend the same method to the synthesis of the unprecedented η^4-silatrimethylenemethane complexes (I, X = SiR_2) starting from alkylidenesilirane (II, X = SiR_2). Here we describe the synthesis of iron and ruthenium complexes of η^4-silatrimethylenemethane and the single-crystal X-ray structure determination of the iron complex. These represent the first isolable conjugated silene systems.[3]

A solution of 1,1-dimesityl-2-(*Z*)-neopentylidenesilirane (**2**) (1.4 mmol)[4] in benzene was stirred with diiron nonacarbonyl (**3a**) (1.6 mmol) for 6 h or refluxed with triruthenium dodecacarbonyl (**3b**) (1.8 mmol) for 12 h. After removal of the solvent in vacuo, the residue was purified by preparative TLC and recrystallization from hexane to provide air- and moisture-stable complexes with the stoichiometry $Mes_2{}^tBuSiC_3H_3M(CO)_3$ (M = Fe, **1a**, 59%; M = Ru, **1b**, 17%) (Scheme II). Whereas the molecular formulas and group assignments are based on conventional spectroscopic techniques and microanalysis, compounds **1a** and **1b** exhibit nearly identical spectroscopic properties.[5] The IR absorptions for the terminal carbonyl ligands of **1a** and **1b** appear as two distinct peaks in the region from 1950 to 2050 cm^{-1}. With increasing wave number, the first is a broad, intense peak and the second is a sharper, less intense peak, which are characteristic of C_{3v}, $M(CO)_3$ complexes. The unsymmetrical organic ligand substitution causes the three carbonyl ligands to become nonequivalent in the ^{13}C NMR spectra (**1a**, δ 213.56, 213.90, 214.18; **1b**, δ 198.32, 199.94, 200.73). Although **2** contains a mirror plane, which makes the two mesityl rings and two methylene protons equivalent, the ^1H NMR spectra of **1a** and **1b** exhibit five singlets (ratio 2:1:1:1:1) and six singlets (ratio 1:1:1:1:1:1) assigned for the *o*- and *p*-methyl protons, respectively. The protons in the monosubstituted trimethylenemethane $Fe(CO)_3$ complex does not show any geminal couplings but does exhibit long-range trans couplings (*W* coupling).[6b] Therefore the lack of observable coupling between inequivalent methylene and methine protons of **1a** and **1b**[7] supports their being located over an organic ligand having an η^4-trimethylenemethane-type framework, as shown in Scheme II. The three sets of ^{13}C NMR chemical shifts (**1a**, δ 42.93 (CH_2), 73.00 (C), 103.06 (CH); **1b**, δ 36.68 (CH_2), 81.38 (C), 98.57 (CH)) appear at reasonably higher field owing to metal coordination. Of particular interest are the ^{29}Si chemical shift values of 43.55 ppm for **1a** and 40.12 ppm for **1b**, which occur at considerably lower field than the shifts for other silene complexes.[1i-k] Very similar values are observed for isolated silenes $(Me_3Si)_2Si{=}C(OSiMe_3)R$ (41.4-54.3 ppm).[8a] Overall the spectroscopic data are consistent with formulation as η^4-silatrimethylenemethane complexes.

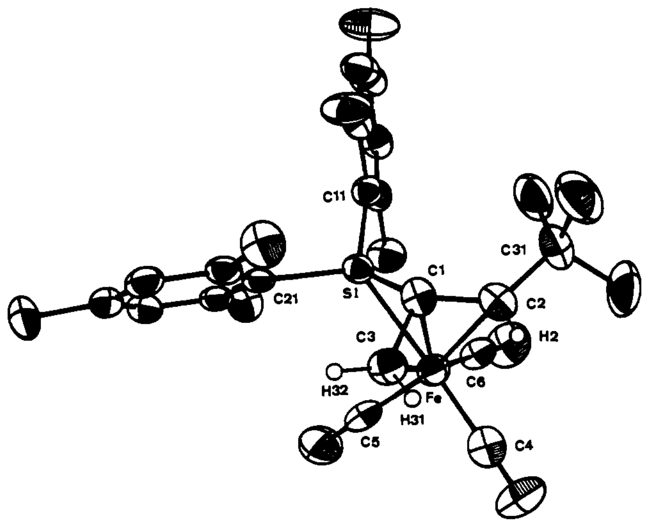

Figure 1. ORTEP drawing of **1a**. Selected bond lengths (Å) and angles (deg): Si–C(11), 1.899 (8); Si–C(21), 1.921 (7); C(2)–C(31), 1.51 (1); C(2)–H(2), 1.0 (1); C(3)–H(31), 1.07 (9); C(3)–H(32), 1.0 (1); Fe–Si, 2.422 (2); Fe–C(1), 1.993 (8); Fe–C(2), 2.182 (9); Fe–C(3), 2.107 (8); Si–C(1)–C(2), 127.8 (6); Si–C(1)–C(3), 106.5 (6); C(2)–C(1)–C(3), 109.6 (7); C(1)–Si–C(11), 126.6 (4); C(1)–Si–C(21), 110.9 (3); C(11)–Si–C(12), 109.1 (3); C(1)–C(2)–C(31), 133.0 (8); C(1)–C(2)–H(2), 107.0 (6); C(31)–C(2)–H(2), 110.0 (5); C(1)–C(3)–H(31), 122.0 (5); C(1)–C(3)–H(32), 122.0 (6); H(31)–C(3)–H(32), 97.0 (8); Si–C(1)–Fe, 78.2 (3); C(2)–C(1)–Fe, 77.5 (5); C(3)–C(1)–Fe, 73.4 (5).

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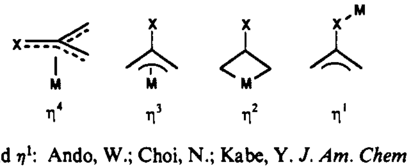
(2) Unlike the trimethylenemethane complex, a variety of hapto modes are discussed with hetero trimethylenemethane complexes.



(a) X = S, η^4 and η^1: Ando, W.; Choi, N.; Kabe, Y. *J. Am. Chem. Soc.* **1990**, *112*, 4574. (b) X = O, η^1: Noyori, R. *Acc. Chem. Res.* **1979**, *12*, 61. (c) X = O, η^2: Kemmitt, R. D.; Mckenna, P.; Russell, D. R.; Prouse, L. J. S. *J. Chem. Soc., Dalton Trans.* **1989**, 345. (d) X = O, η^3: Fawcett, J.; Henderson, W.; Jones, M. D.; Kemmitt, R. D. W.; Russell, D. R.; Lam, B.; Kang, S. K.; Albright, T. A. *Organometallics* **1989**, *8*, 1991. (e) X = O, η^3: Trost, B. M.; Schnider, S. *J. Am. Chem. Soc.* **1989**, *111*, 4430. (f) X = O, μ-η^1,η^3-dimers: Frey, M.; Jenny, T. A.; Stoeckli-Evans, H. *Organometallics* **1990**, *9*, 1806. (g) X = O, μ-η^1,η^3: Holmgren, J. S.; Shaply, J. R.; Wilson, S. R.; Pennington, W. T. *J. Am. Chem. Soc.* **1986**, *108*, 508. (h) X = O, η^4 and η^2: Hartwig, J. F.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1990**, *112*, 5670. (i) X = NR, η^3: Ohe, K.; Ishihara, T.; Chatani, N.; Murai, S. *J. Am. Chem. Soc.* **1990**, *112*, 9646.

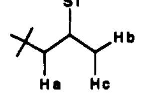
(3) Although pioneering work on an η^3-1-silapropenyl transition-metal complex has been reported, an X-ray structure determination was unsuccessful, as well as spectroscopic assignment being controversial. (a) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1976**, *98*, 7453. (b) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Organomet. Chem.* **1980**, *184*, 13. (c) Radnia, P.; Mckennis, J. S. *J. Am. Chem. Soc.* **1980**, *102*, 6349.

(4) (a) Ando, W.; Saso, H. *Tetrahedron Lett.* **1986**, *27*, 5625. (b) Saso, H.; Ando, W. *Chem. Lett.* **1988**, 1567. (c) Saso, H.; Yoshida, H.; Ando, W. *Tetrahedron Lett.* **1988**, *29*, 4747. (d) Saso, H.; Ando, W.; Ueno, K. *Tetrahedron* **1989**, *45*, 1929.

(5) **1a**: pale brown crystals; mp 174–176 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 0.82 (s, 10 H), 1.42 (s, 1 H), 2.19 (s, 6 H), 2.48 (s, 3 H), 2.67 (s, 3 H), 2.78 (s, 1 H), 2.85 (s, 3 H), 2.89 (s, 3 H), 6.72 (s, 2 H), 6.81 (s, 1 H), 6.89 (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.92 (q), 20.96 (q), 25.42 (q), 25.69 (q), 26.00 (q), 28.09 (q), 31.66 (q), 35.10 (s), 42.93 (t), 73.00 (s), 103.06 (d), 128.35 (d), 128.76 (d), 129.05 (d), 129.28 (d), 130.55 (s), 132.34 (s), 138.86 (s), 139.62 (s), 143.01 (s), 143.18 (s), 143.75 (s), 145.82 (s), 213.56 (s), 213.90 (s), 214.18 (s); ^{29}Si NMR (18 MHz, $CDCl_3$) δ 43.55; IR (KBr) ν 2028 (s), 1959 (br) cm^{-1}; MS, *m/z* 502 (M^+), 474 ($M^+ - CO$), 446 ($M^+ - 2CO$), 418 ($M^+ - 3CO$); HRMS calcd for $C_{28}H_{34}O_3SiFe$ 502.1627, found 502.1596. Anal. Calcd: C, 66.93; H, 6.82. Found: C, 66.90; H, 6.70. **1b**: pale brown crystals; mp 139–141 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 0.81 (s, 9 H), 0.93 (s, 1 H), 1.44 (s, 1 H), 2.18 (s, 3 H), 2.19 (s, 3 H), 2.51 (s, 3 H), 2.67 (s, 3 H), 2.90 (s, 3 H), 2.91 (s, 3 H), 2.97 (s, 1 H), 6.71 (s, 1 H), 6.72 (s, 1 H), 6.78 (s, 1 H), 6.89 (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.90 (q), 20.95 (q), 25.29 (q), 26.28 (q), 28.62 (q), 32.75 (q), 34.12 (s), 36.68 (t), 81.38 (s), 98.57 (d), 128.36 (d), 128.59 (d), 129.00 (d), 129.08 (d), 131.66 (s), 132.41 (s), 138.30 (s), 139.24 (s), 142.69 (s), 143.11 (s), 143.73 (s), 145.24 (s), 198.32 (s), 199.94 (s), 200.73 (s); ^{29}Si NMR (18 MHz, $CDCl_3$) δ 40.12; IR (KBr) ν 2054 (s), 1992 (br), 1970 (br) cm^{-1}; MS, *m/z* 548 (M^+), 520 ($M^+ - CO$), 492 ($M^+ - 2CO$), 464 ($M^+ - 3CO$), 362 ($M^+ - Fe(CO)_3$); HRMS calcd for $C_{28}H_{34}O_3SiRu$ 548.1321, found 548.1345.

(6) (a) Churchill, M. R.; Gold, K. *J. Chem. Soc., Chem. Commun.* **1968**, 693. (b) Ehrlich, K.; Emerson, G. E. *J. Am. Chem. Soc.* **1972**, *94*, 2464.

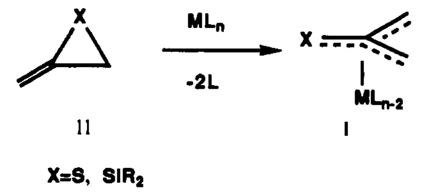
(7) In the C–H COSY spectra of **1a** and **1b**, the methylene carbons showed the cross peaks to Hc (**1a**, δ 0.82; **1b**, δ 0.93) and Hb (**1a**, δ 1.42; **1b**, δ 1.44) labeled in the order of increasing chemical shift. A reasonable NOE between



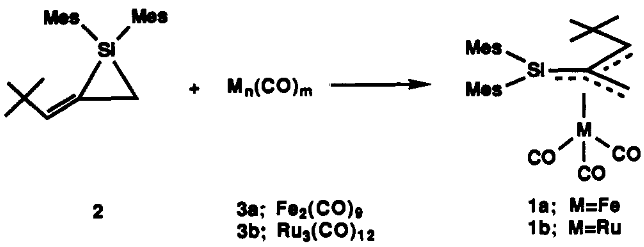
Ha (**1a**, δ 2.78; **1b**, δ 2.97) and Hc except for geminal Hb and Hc in NOESY spectra unambiguously established configurational assignment of Ha, Hb, and Hc.

(8) (a) Brook, A. G.; Abdesaken, F.; Gutekunst, G.; Plavec, N. *Organometallics* **1982**, *1*, 994. (b) Wiberg, N.; Wagner, G.; Muller, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 229.

Scheme I



Scheme II



Conclusive evidence was obtained from an X-ray analysis. Recrystallization of the iron analogue (**1a**) from hexane at 0 °C yielded well-formed prisms. The molecule crystallized in space group *Pna*2₁; an ORTEP drawing is shown in Figure 1 together with selected bond lengths and angles.[9] The silatrimethylenemethane ligand is bound in an η^4 fashion and staggered relative to the three carbonyl ligands. The bond distances C(1)–Si, C(1)–C(2), and C(1)–C(3) are 1.840 (8), 1.42 (1), and 1.46 (1) Å, which falls midway between C–Si or C–C single and double bonds.[8] Especially the C(1)–Si distance is somewhat longer than the values found in other silene complexes:[1i-h] $Cp^*RuHPCy_3(\eta^2\text{-}CH_2{=}SiMe_2)$, 1.78–1.79 Å; $Cp^*IrPMe_3(\eta^2\text{-}CH_2{=}SiPh_2)$, 1.810 Å; $Cp_2W(\eta^2\text{-}CH_2{=}SiMe_2)$, 1.800 Å. The cross-conjugative interaction with the C–C double bond may be responsible for the slightly longer values of the C(1)–Si bond. The methylene and methine protons in **1a** were located and refined, allowing discussion of the nonplanarity of the ligand. The sum of the angles around silicon and the three carbons C(1), C(2), and C(3) are 346.6°, 343.9°, 350°, and 341°, between the 360° and 329.1° values expected for sp^2 and sp^3 hybridization. The central carbon C(1) lies above the plane of the other three atoms, while planes containing C(11)–Si–C(12), C(31)–C(2)–H(2), and H(31)–C(3)–H(32) are bent away from the $Fe(CO)_3$ fragment. Thus, the η^4-silatrimethylenemethane ligand adopts an umbrella shape, as it is in the structurally characterized trimethylenemethane[6b] and its hetero analogue.[2a,h] The low yield realized for **1b** is in part due to the competitive formation of an alkylidenesilirane-containing triruthenium complex, which structure will be reported elsewhere.

The successful construction of title complexes **1a** and **1b** suggests the ring opening of hetero-analogous methylenecyclopropane and η^4-complexation by transition metals to be more general than expected.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (No. 02230101) from the Ministry of Education, Science and Culture, Japan.

Supplementary Material Available: Detailed information on the X-ray crystal analysis of **1a** and 2D NMR spectra of **1a** and **1b** (21 pages); listing of observed and calculated structure factors for **1a** (5 pages). Ordering information is given on any current masthead page.

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[9] Crystal data for **1a**: $C_{28}H_{34}O_3SiFe$, $M = 502.51$, orthorhombic with $a = 10.254$ (2) Å, $b = 14.402$ (2) Å, $c = 18.151$ (3) Å, $V = 2680.5$ Å^3, space group *Pna*2₁, $Z = 4$, $\mu(\text{Mo K}\alpha) = 6.3\ \text{cm}^{-1}$, $\rho_{\text{calcd}} = 1.25\ \text{g/cm}^3$. The 1710 independent reflections [$2\theta \le 50°$; $|F_o^2| > 3\sigma|F_o^2|$] were measured on an Enraf-Nonius CAD4 diffractometer using Mo Kα irradiation and an ω–2θ scan. The structure was solved by direct methods, and all non-hydrogen atoms were refined anisotropically and hydrogen atoms refined with fixed thermal parameters to $R = 0.044$ and $R_w = 0.048$.

Regioselectivities and Stereoselectivities of Singlet Oxygen Generated by Cyclodextrin Sandwiched Porphyrin Sensitization. Lipoxygenase-like Activity

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Singlet oxygen has been attracting significant attention from physical and organic chemists due to its unique properties, and various types of reactions involving this highly reactive molecular oxygen have been investigated.[1] Although some of these reactions are very useful even for synthetic purposes, the reactions are usually nonregio- and/or nonstereoselective because of the high reactivity of singlet oxygen. For example, oxidation of linoleic acid by singlet oxygen results in nonselective oxidation of the $\Delta^{9,10}$ and $\Delta^{12,13}$ double bonds to give 9-, 10-, 12-, and 13-hydroperoxy derivatives as ene reaction products.[2] This observation is quite in contrast with that for biological oxidation catalyzed by enzymes such as dioxygenase which gives hydroperoxy products in regio- and stereospecific fashion; for example, soybean lipoxygenase exclusively produces L-13-hydroperoxy-9,11-*cis*,*trans*-octadecadienoate from linoleic acid.[3]

We report here the first example of regio- and stereospecific oxidation of linoleic acid by singlet oxygen which is generated by cyclodextrin sandwiched porphyrin sensitization. Although both specificities are still not perfect, the present results suggest the interesting possibility of reaction control of singlet oxygen.

The cyclodextrin sandwiched porphyrin used here is an equimolar mixture of diagonal type isomers (**1a** and **1b**).[4] Tetrakis(*p*-sulfonatophenyl)porphyrin (**2**) is also used as a reference sensitizer having no substrate binding site (Figure 1).

The major products of present reactions are hydroperoxy dienes **4a–d**, and the trans,trans isomers corresponding to **4a** and **4d** are also detected as the minor rearranged products as reported previously.[2] The results are summarized in Table I together with experimental details.

The most remarkable result is obtained when nearly equimolar amounts of **1** and the substrate are employed (run 6), i.e., the hydroperoxidation takes place selectively at the $\Delta^{12,13}$ double bond to yield **4a** and **4b** in 82% specificity [(**4a** + **4b**)/total].[5] The product distribution, **4a**/**4b**/**4c**/**4d** (51/31/11/7), indicates that the attack of singlet oxygen in the present system is more facile at the position remote from the carboxyl end of **3**. The importance of the binding sites of the cyclodextrin in the present reaction is clearly shown by the observation that, as expected, sensitization by a simple water-soluble porphyrin, **2** (runs 1–3), results in nonselective hydroperoxidation at the $\Delta^{9,10}$ and $\Delta^{12,13}$ double bonds, though the product ratios **4a**/**4b** and **4c**/**4d** vary according to the reaction conditions.[2] It should be noted that a combination of **2** as a sensitizer and a large excess of β-cyclodextrin as a complexation host does not change the nonselective reaction course of singlet oxygen generated by sensitization with **2** (run 4). These observations strongly suggest that the existence of both **3** and

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[5] The product ratios including trans,trans isomers corresponding to **4a** and **4d**, **4a**/*trans*,*trans*-**4a**/**4b**/**4c**/**4d**/*trans*,*trans*-**4d**, are 49/3/30/10/7/1 for run 6 and 31/1/18/17/31/2 for run 5, respectively.

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